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NEODYMIUM LASER GLASS
IMPROVEMENT PROGRAM

Technical Summary Report
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American Optical Company
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ILLUSTRATIONS

1. INTRODUCTION

This report is a technical summary covering work performed in the period between 30 June 1963 and 30 June 1964 on Contract Nonr-3835(00) entitled Laser Materials Research and Development. During this period, we have carried out investigations in the following areas: (1) laser glass compositions which are non-solarizing, (2) the effect of host glass composition on fluorescent lifetime, (3) analysis of the fluorescent decay curve and (4) laser threshold studies.

This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

2.   TECHNICAL DISCUSSION

2.1   SOLARIZATION

A limited amount of additional work has been done on
the study of solarization (an increase in the absorption of a
glass resulting from its exposure to light) produced by xenon
flashtubes. This is of interest because of the obvious effect
of absorption in the 1 micron region on laser emission and because
absorption in the visible region not only decreases the pumping
efficiency but also produces undesired thermal gradients in the
laser rod.

The effects of Sb_2O_3, TiO_2 and CeO_2 on solarization,
singly and in combination, have been investigated. The Nd_2O_3 was
omitted in these glasses so that its absorption bands would not
mask the effects resulting from solarization. Figure 1 shows the
effect of the addition of 1 wt.% of the above oxides to a base
glass with the following wt.% composition: SiO_2, 72%; Na_2O, 7.5%;
K_2O, 11.5%; Li_2O, 1%; BaO, 5%; Al_2O_3, 1.5% and ZnO, 1.5%. The
presence of Sb_2O_3 in the glass prevents absorption due to solari-
zation in the rod region above 500 mμ but not in the blue. There
are some indications that it may actually promote solarization in
the 350 to 400 mμ region. The glass containing TiO_2 exhibits a
gradual decrease in solarization across the whole visible region
in the direction of increasing wavelength. The degree of solari-
zation varies inversely with the amount of TiO_2 present in the glass
as shown in Fig. 2 in which glasses containing 1% and 3% TiO_2 are
compared. Cerium oxide, also shown at 1% concentration, appears
to be a more effective agent than either Sb_2O_3 or TiO_2 in
preventing solarization when used alone.

The effect of Sb_2O_3 plus TiO_2 and/or CeO_2 was investi-
gated since Sb_2O_3 (or As_2O_3) is usually added to the glass as a
"fining" agent to aid in the removal of bubbles from the glass
during melting. The addition of 1 wt.% Sb_2O_3 to the TiO_2 glasses
combines the good features of each. The Sb_2O_3 eliminates the
solarization present in the red region of the TiO_2 glasses and the
two combine to decrease the solarization in the blue region for a
1% TiO_2 glass and eliminate it in the 3% TiO_2 glass as shown in
Fig. 3.

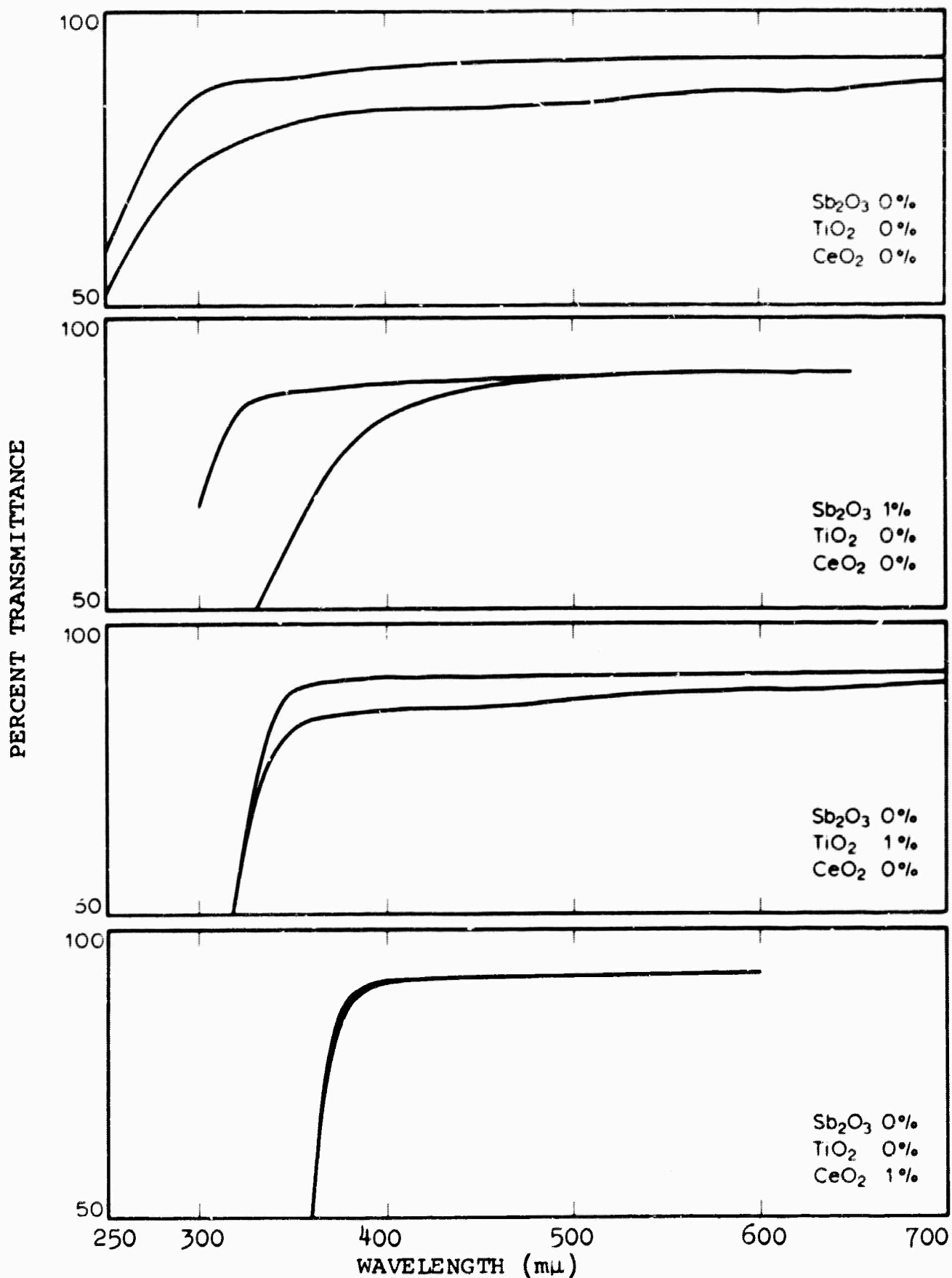Figure 1. The Effect of Sb_2O_3, TiO_2 and CeO_2 on the Solarization of a Potassium-Barium-Silicate Glass. The Solarized Curve is the Lower One in Each Case.
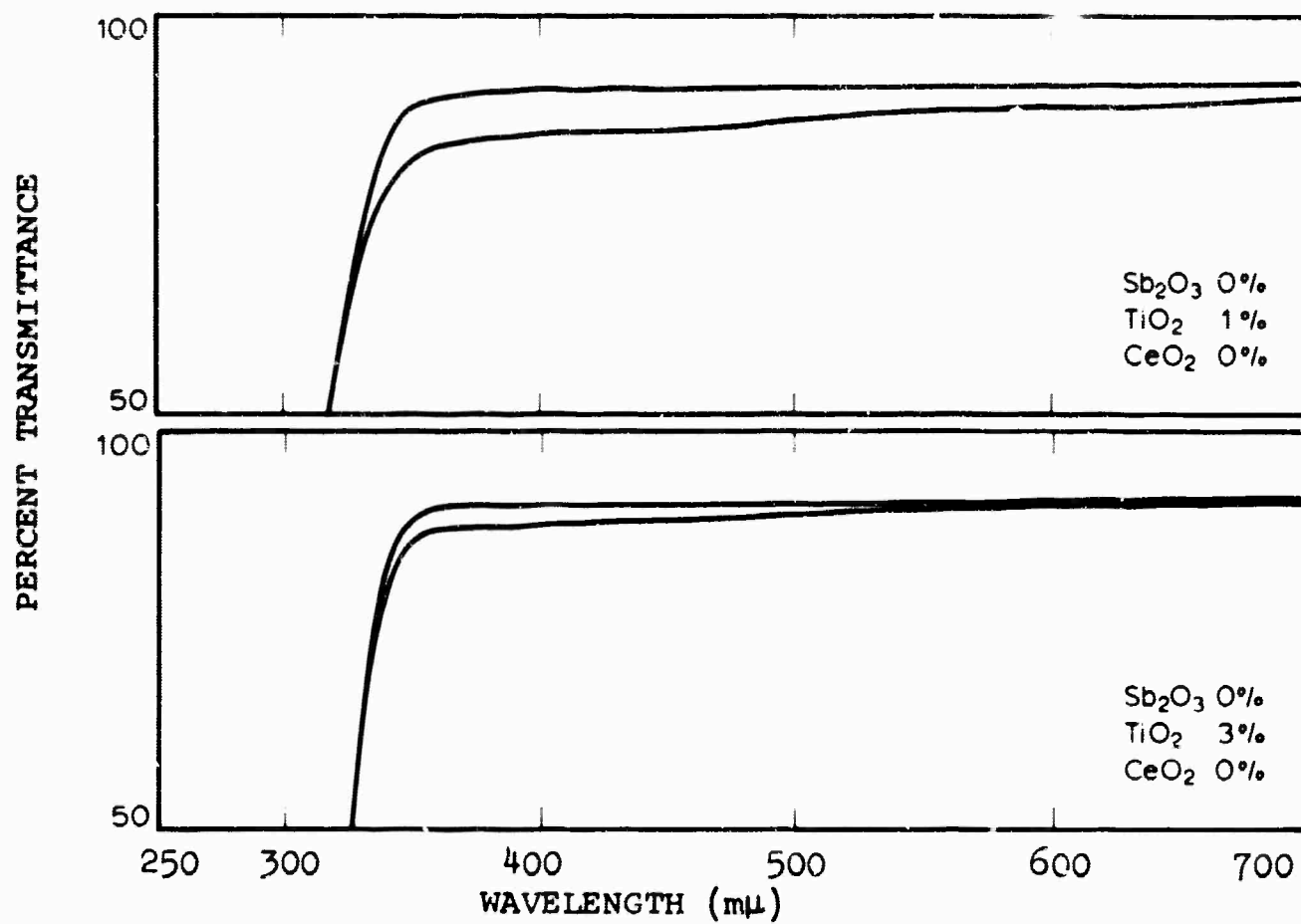
Figure 2. The Effect of Increasing TiO_2 Concentration From 1 to 3% in a Potassium-Barium-Silicate Glass.
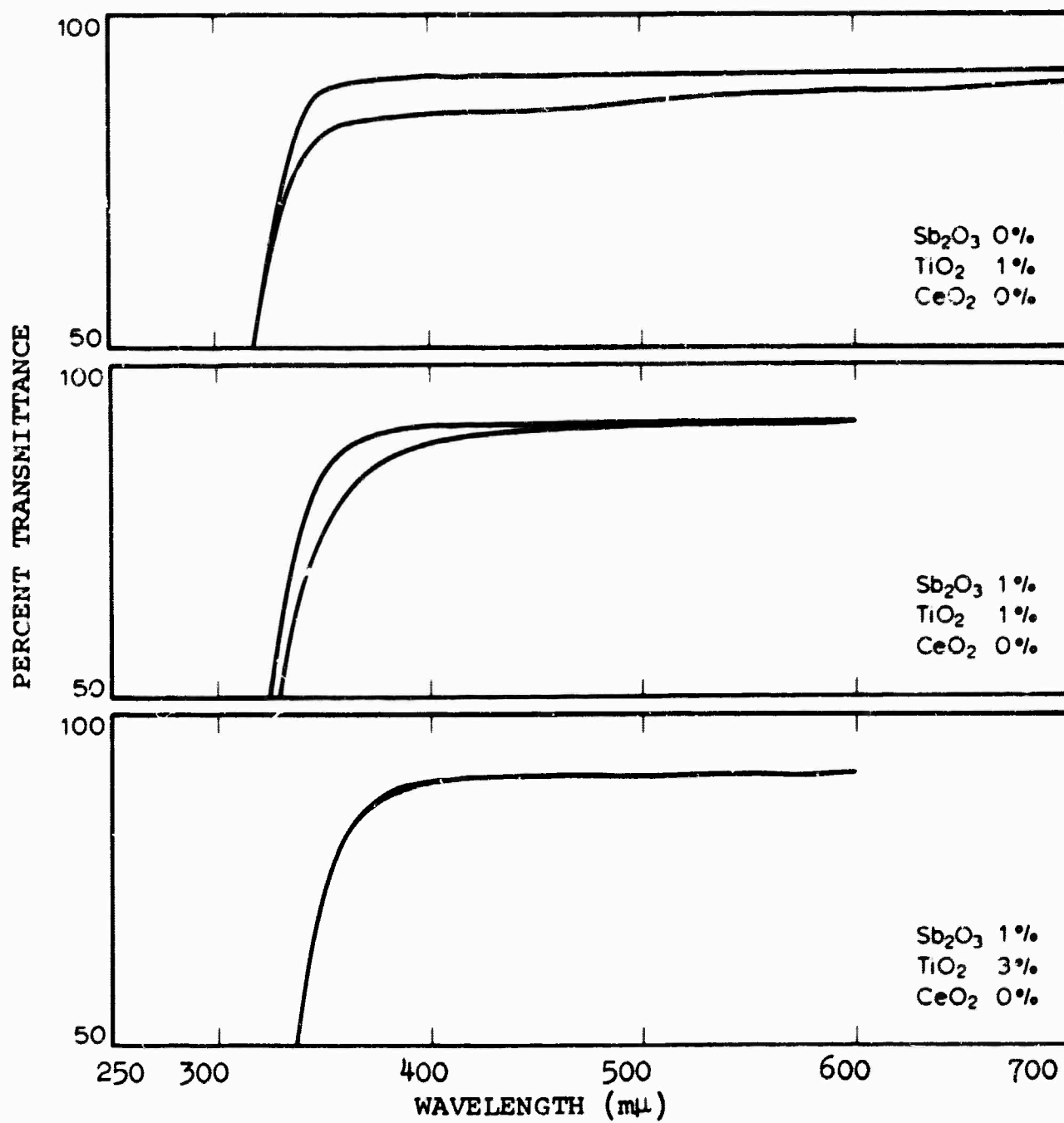
Figure 3. The Effect on Solarization of the Addition of Sb_2O_3 to a Potassium-Barium-Silicate Class Containing TiO_2.

The addition of Sb_2O_3 to the 1 wt.% CeO_2 glass intro-
duces the solarization in the blue region characteristic of the
Sb_2O_3 glass. This is decreased but not removed by increasing the
CeO_2 content from 1 wt.% to 3 wt.% as shown in Fig. 4. The
addition of Sb_2O_3 to the glasses containing both TiO_2 and CeO_2
has very little effect as shown in Fig. 5.

It seems reasonable to expect that the absorption cutoff
wavelength might have some effect on the degree of solarization
(due to the total amount of ultraviolet radiation penetrating the
glass) and on the wavelength at which solarization takes place
(due to the possible existence of energy thresholds in the
solarizing mechanism). There are indications of the former in
Fig. 1 where the degree of solarization appears to decrease as
the cutoff wavelength moves further toward the visible region.

This fails to explain the situation completely, however,
since the glass containing 1% Sb_2O_3 and 3% TiO_2 with a cutoff
(50% transmission) at 337 mμ shows no solarization whereas the
one containing 1% Sb_2O_3 and 3% CeO_2 with a cutoff at 367 mμ shows
appreciable solarization. It would appear that other conditions
must be taken into account to fully explain this behavior. The
changes introduced by the presence of Sb_2O_3 may possibly be
explained on the basis of changes in the oxidizing conditions
of the melt which in turn effects the solarization[1,2].

2.2   FLUORESCENT LIFETIME

The fluorescent lifetime data has been analyzed to
see if any correlation exists between lifetime and composition.
Sixteen of the more commonly used oxides were included in this
analysis which covered 300 glasses. The following equation
provided the best agreement between calculated and experimental
values of lifetime:

$$\tau = 0.461 + A_{SiO_2}C_{SiO_2} + \sum_n \frac{A_n C_n}{C_{SiO_2}}$$

where τ is the lifetime in milliseconds, C_n is the concentration
of a given oxide (n) in weight percent and A_n is the correlation
coefficient which establishes the relationship between composition
and lifetime. The oxides included in the study, their coefficients
and standard deviations, σ_n, are given in Table I. The coef-
ficients for K_2O, ZrO_2 and Sb_2O_3 have small absolute values which
are less than the standard deviation and therefore they were
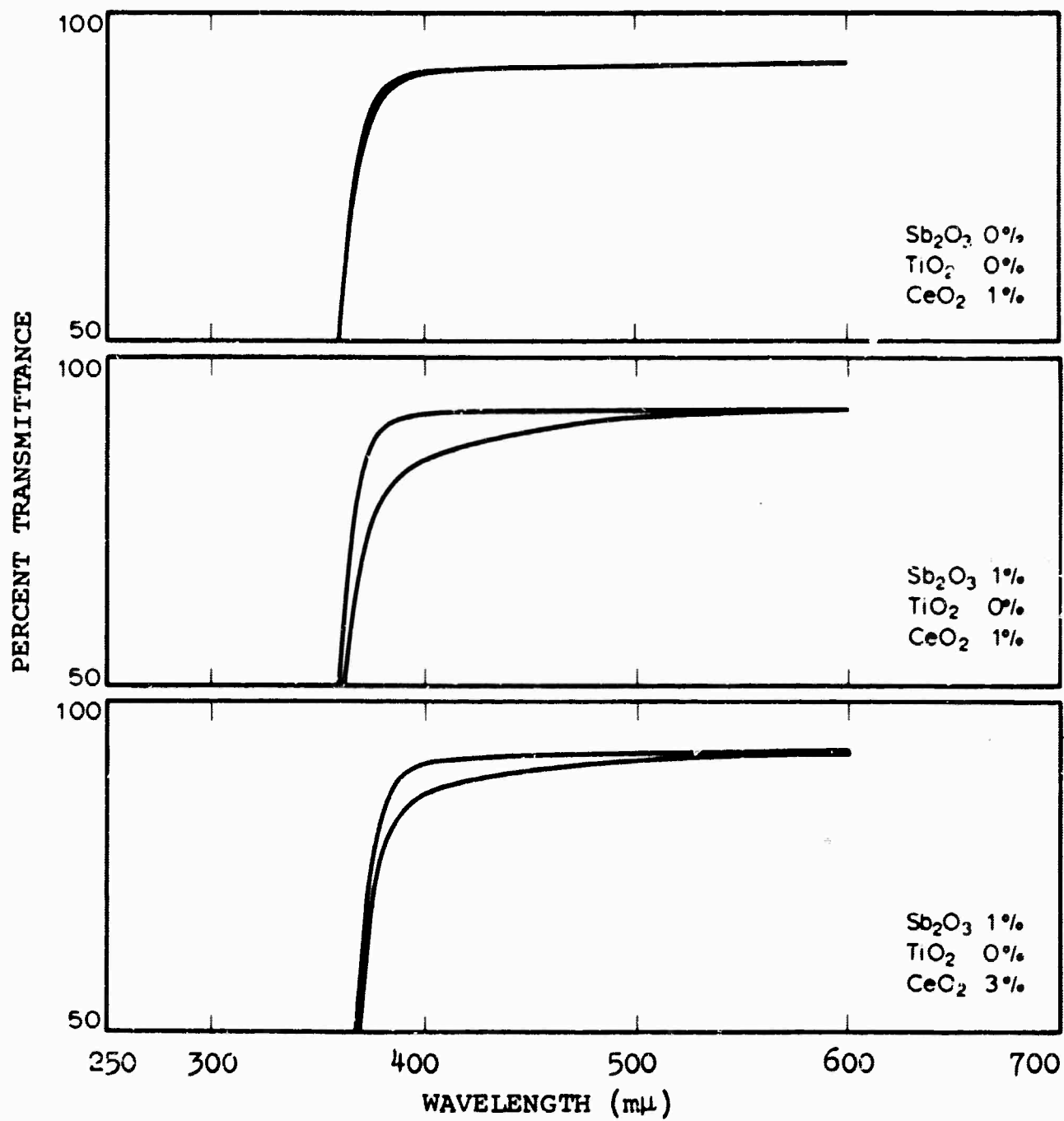considered to be zero in this analysis.

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Figure 4. The Effect on Solarization of the Addition of Sb_2O_3 to a Potassium-Barium-Silicate Glass Containing CeO_2 .
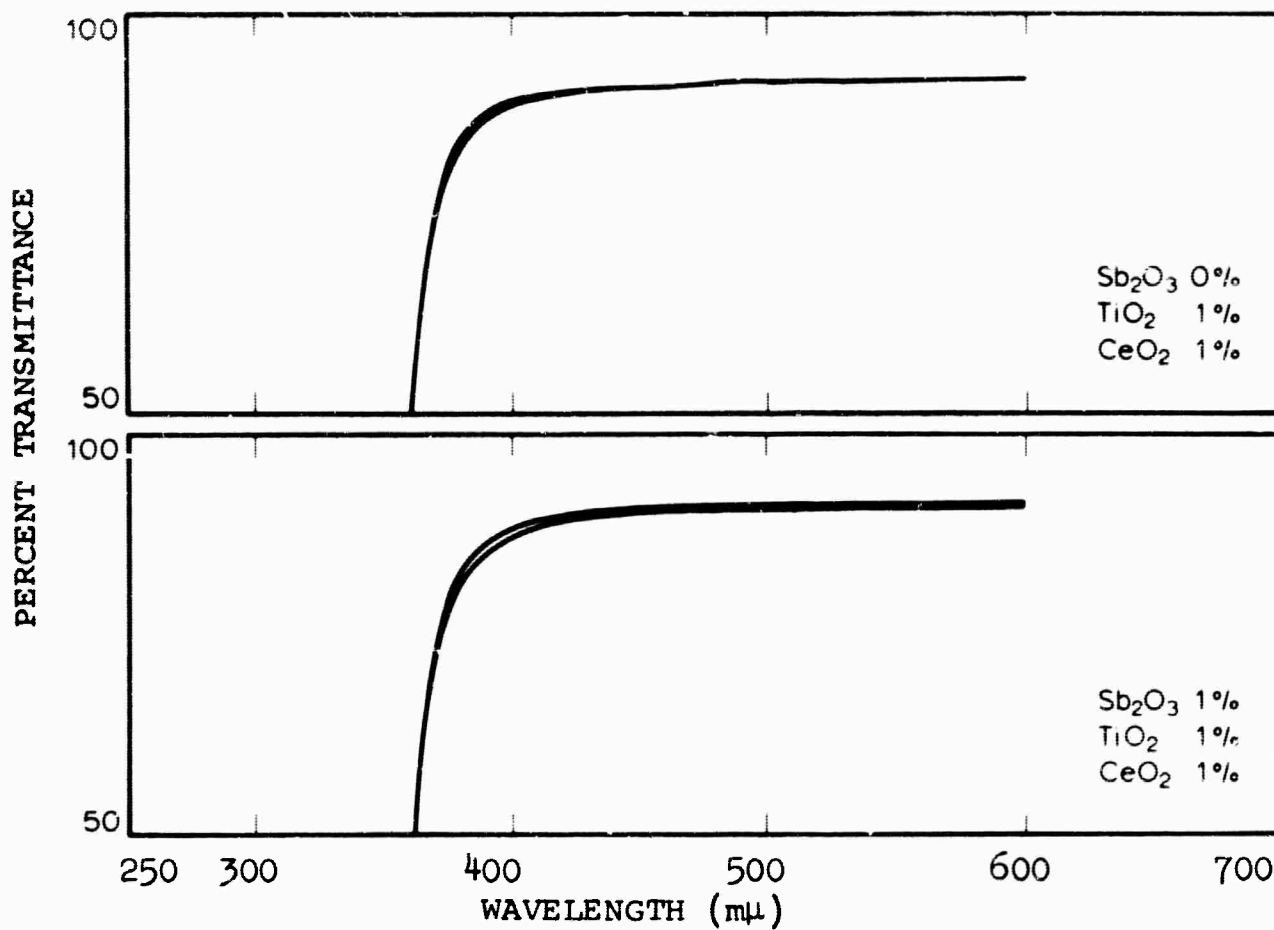
Figure 5. The Effect on Solarization of the Addition of Sb_2O_3 to a Potassium-Barium-Silicate Glass Containing Both TiO_2 and CeO_2.

TABLE I

Periodic Group	n (oxide)	λ_n (correlation coefficient)	σ_n (standard deviation)
I A	Li_2O	− 1.288	0.291
	Na_2O	− 0.619	0.074
	K_2O	∼ 0	
	Rb_2O	0.167	0.036
	Cs_2O	0.138	0.040
II A	MgO	− 1.054	0.215
	CaO	− 1.025	0.109
	BaO	− 0.259	0.046
II B	ZnO	− 1.555	0.100
III A	Nd_2O_3	− 1.567	0.422
	$(Nd_2O_3)^2$	− 5.599	3.94
	$(Nd_2O_3)^3$	27.7	9.67
III B	B_2O_3	− 0.980	0.308
	Al_2O_3	− 1.223	0.378
IV A	TiO_2	− 0.452	0.158
	ZrO_2	∼ 0	
IV B	SiO_2	0.592	0.136
	PbO	− 0.115	0.032
V B	Sb_2O_3	∼ 0	

The standard (r.m.s.) deviation between experimental and calculated values of τ is $\pm$ 0.08 ms. A small amount of this error may be attributed to the experimental data itself which is reproducible to about $\pm$ 0.01 ms. The main cause of this deviation, however, is due to the limited accuracy of the correlation coefficients. The standard deviations of these coefficients have values that are 10 to 30% of the value of the coefficients themselves. Assuming a Gaussian distribution where 68% of the values fall within the limits of the standard deviation this means that in the case of silica for example where A_n = 0.592 $\pm$ 0.136, 68% of the glasses predict a coefficient between .456 and .728

and the remaining 32% of the glasses predict coefficients which exceed these limits. Despite the fact that these coefficients leave something to be desired in the way of accuracy, the data in Table I is significant in that a definite correlation between composition and lifetime may be observ'd here; namely, the correlation coefficient becomes more positive (lifetime increases) as the atomic number increases in any given periodic group, i.e. Li to Cs. The notable exceptions are B_2O_3 in group III B and SiO_2 in IV B. These two oxides differ from the other oxides in the Table in that they are both strong glass "network formers" whereas the other oxides tend to be "network modifiers".

One of the factors affecting the accuracy of the correlation coefficients and thus the agreement between experimental and calculation values of τ is the assumption in the above analysis that the relationship between the concentration of a given oxide and lifetime is a linear one, with the exception of Nd_2O_3 which was known to be nonlinear from previous experience. This assumption is not always valid, particularly at high concentrations of the group I A oxides as shown in Fig. 6. Curves of lifetime vs. concentration such as those plotted here are necessary when more detailed information about this relationship is required. Each curve represents a series of glasses in which the oxide being studied is substituted for silica only and the concentrations of the other ingredients are kept constant. The lifetime scale is shown here in arbitrary units since the base glass, although fixed for a given series, cannot be the same for each series. It is for this same reason of changing base glass that this detailed information on lifetime vs. the concentration of a specific oxide it is not sufficient by itself to provide correlation coefficients such as those above.

The curves for the group I A oxides, which are of most interest because they do have some areas with a positive slope, are unfortunately the least linear. At the higher concentrations they level off or go through a maximum. The group II A oxide curves appear to be quite linear tailing off slightly at high concentrations. The other curves are also linear but the range of concentration is not very large.

2.3   FLUORESCENT DECAY CURVE ANALYSIS

The shape of the fluorescent decay curve has been studied to gain some insight regarding the nature of the neodymium ion sites.
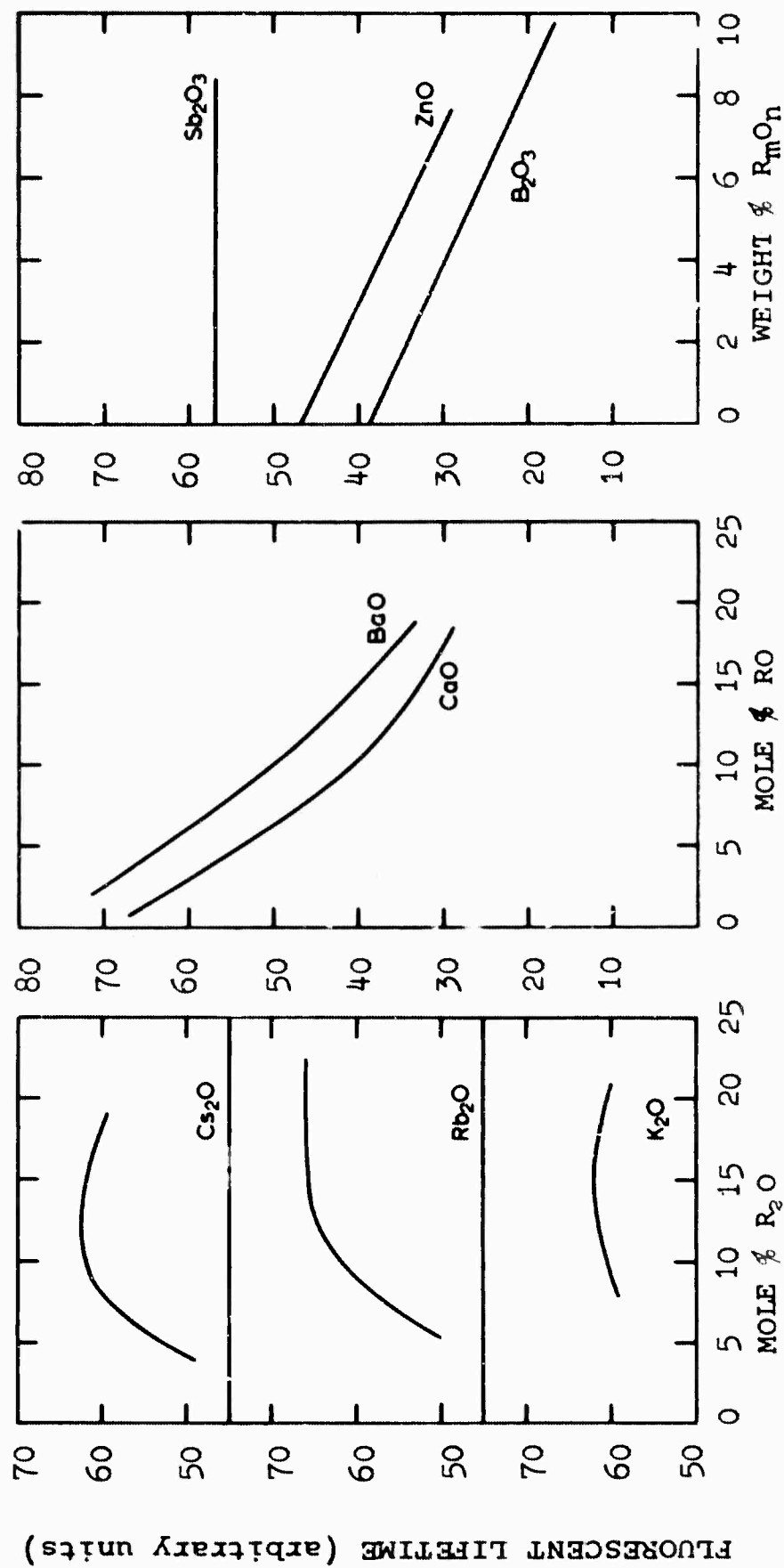
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Figure 6. Lifetime vs. Concentration Curves for Several Oxides. All Substitutions are at the Expense of Silica.

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The curve of fluorescent light intensity vs. time is not a pure exponential curve as would be expected in a simple decay process. The approach being taken is to resolve the observed decay curve into two or more pure exponential curves represerting the fluorescent emission from neodymium ions having two or more different environments. This type of analysis can be performed only when the individual decay processes making up the composite curve are independent of each other, i.e. that there is no interaction between neodymium sites. Since one of the proposed mechanisms for concentration quenching is the transfer of an excited state from one neodymium ion to a neighboring neodymium ion, the above type of analysis predicts that individual exponential components of the observed curve will lose their identity as the Nd_2O_3 concentration is increased to the point where concentration quenching takes place.

The apparatus used in these measurements is a slightly modified version of the standard fluorescent lifetime measuring equipment which consists of a short pulse xenon source and a photomultiplier detector plus suitable filters to insure that only fluorescent light enters the detector. A chopper has been added as shown in Fig. 7 which permits the examination of the very low light intensity portions of the tail of the fluorescence curve, where high gain is required, without saturating the detector with light from the initial, high intensity portion of the curve where the intensities may be 100 to 1000 times greater.

The results indicate that there is little or no association between neodymium sites and specific ingredients in the glass; e.g. one value of decay lifetime is not associated with a potassium-influenced site and another lifetime associated with a barium-influenced site such that the composite curve becomes a function of composition. This is illustrated in Table II which gives the lifetimes of the two individual decay processes which make up the observed decay curves for three barium crown glasses in two of which cesium and rubidium have been substituted for potassium in part.

TABLE II

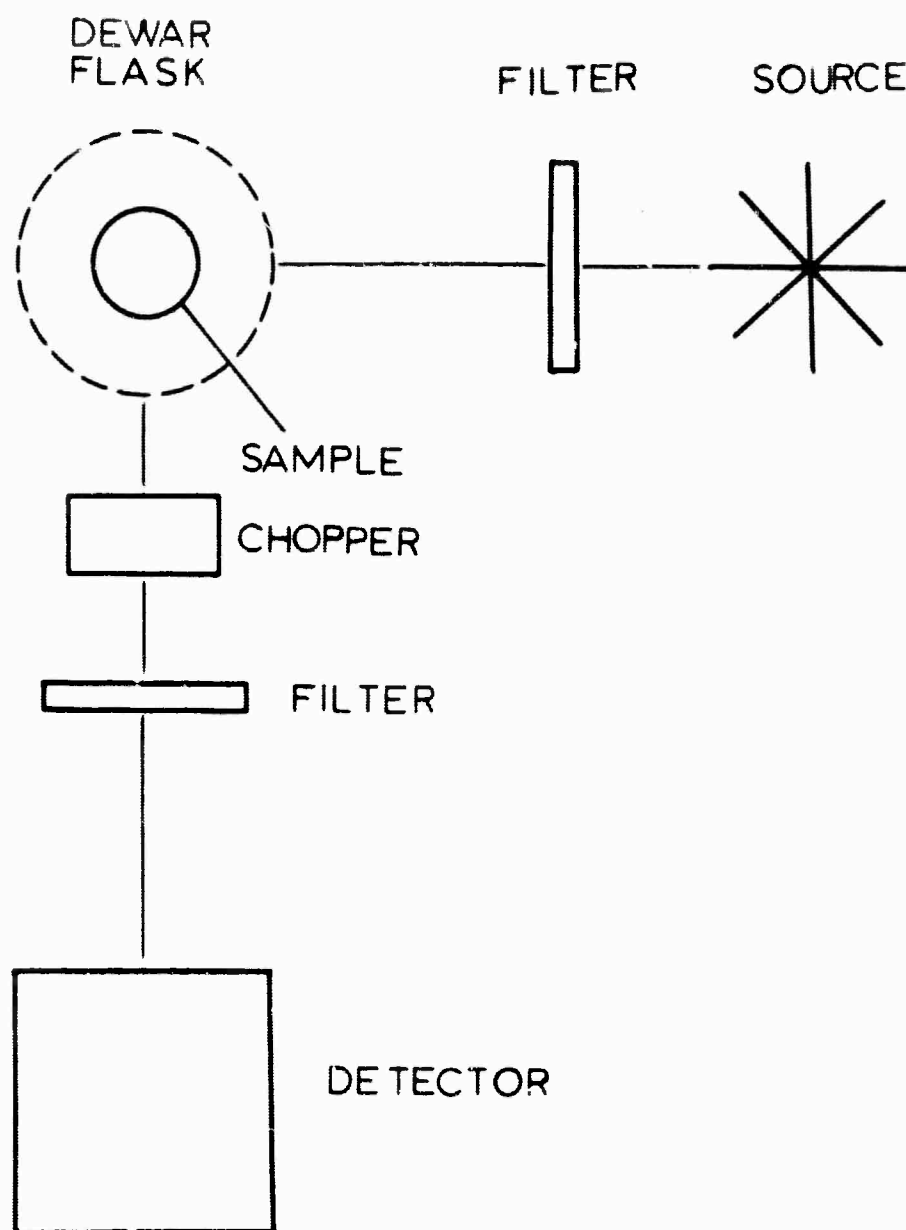| Composition in mole %							τ_1	τ_2
SiO_2	K_2O	Rb_2O	Cs_2O	BaO	Sb_2O_3	Nd_2O_3		
65.7	21.8	----	----	10.9	.5	1	.57	.20
73.3	19.8	3.3	----	2.0	.4	1.1	.89	.37
77.9	13.9	----	4.6	2.1	.4	1	.97	.42

Figure 7. Schematic Diagram of the Apparatus Used to Study the Shape of the Fluorescent Decay Curve.

If the above association between lifetime and composition existed one might expect a slight shift in one of the lifetimes due to the partial replacement of K_2O by Rb_2O or Cs_2O but not a change in both lifetimes of the magnitude observed. These results are best explained by assuming all sites in a given base glass to be essentially the same but due to statistical chance or crystal habit of the neodymium oxide some sites are doubly occupied or are closely enough coupled to introduce a second lifetime. There are additional pieces of data which indicate that the values of τ_1 and τ_2 and the relative number τ_1 sites vs. τ_2 sites vary with composition of the base glass due to its effect upon the crystal field within the glass, i.e. due to the "tightness" of the host lattice as a whole, but not through association with specific ingredients in the glass.

Lifetime properties are obtained from curves such as those shown in Fig. 8. The intensity of fluorescent light is plotted on the log axis in arbitrary units and time along the linear axis so that true exponentials can be represented as straight lines.

The curves on the left are plots of the experimental data. The straight tail of the curve is assumed to be due to the long lifetime component only, the short lifetime sites being emptied by this time. The slope of this straight portion provides a value τ_1 for the long lifetime sites. Extrapolating this portion back to $t = 0$ (as shown by the dotted line in Fig. 8) yields a value of I_{10}, the initial light intensity due to long lifetime sites. The intensity difference between the experimental curve and the τ_1 line represents the light intensity due to the short lifetime sites which is replotted on the right hand side of Fig. 8. The lifetime value, τ_2, and the initial light intensity, I_{20}, of the short lifetime sites are obtained from the slope and intercept of the ordinate axis, respectively, of these generated curves.

The curves in Fig. 8 were obtained at $77°K$ for a potassium-barium-silicate base glass containing 0.5, 2.5, 5 and 7.5 wt.% Nd_2O_3. Previous data indicates that glasses with the same base containing 1% Nd_2O_3 or less produce the same results as the 0.5% Nd_2O_3 glass. Data obtained from the above curves are listed in Table III.
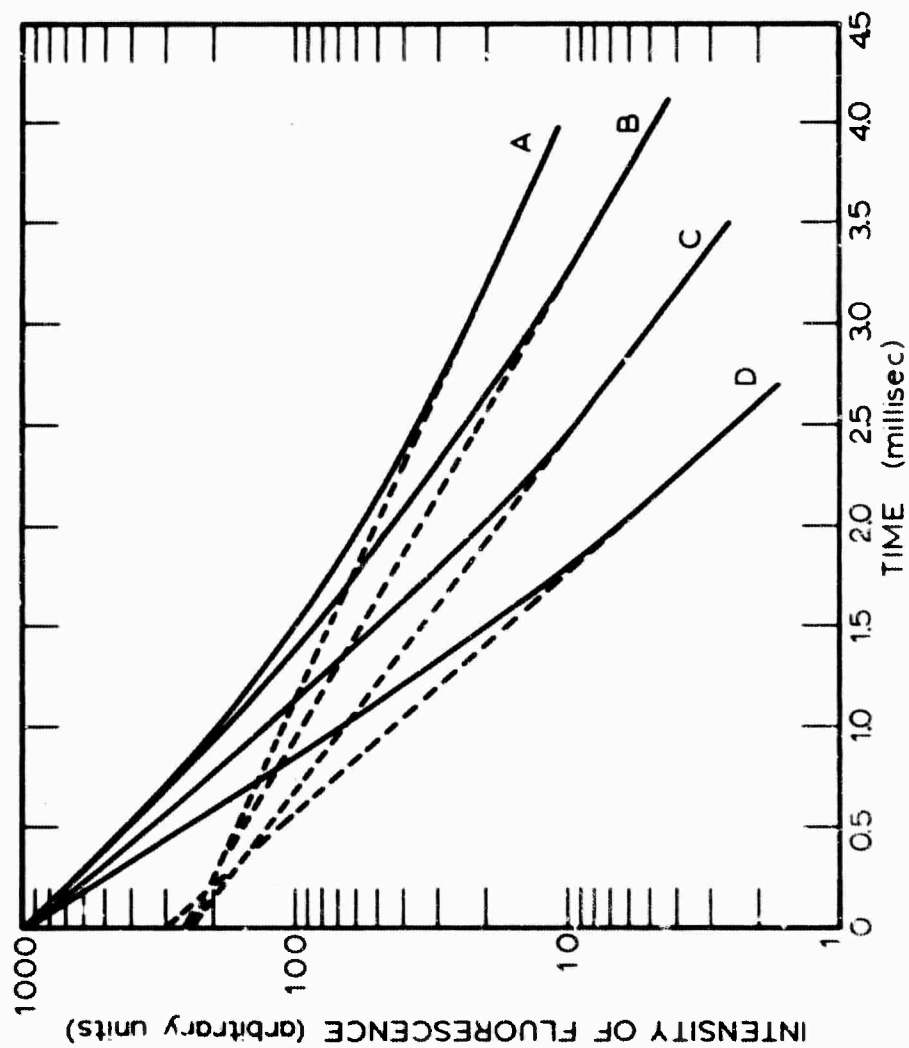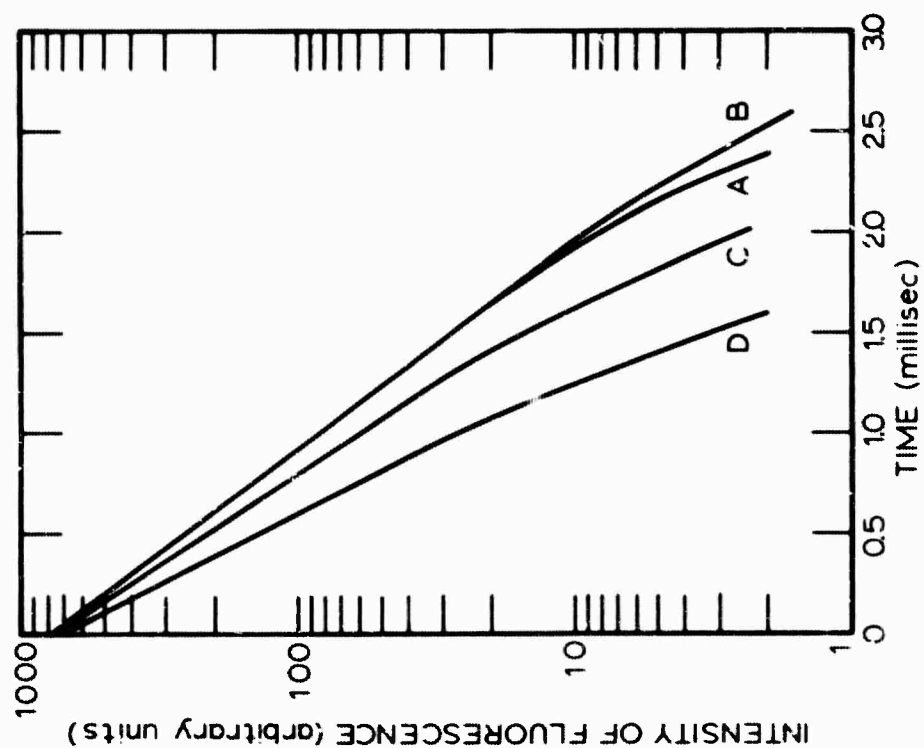
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Figure 8. ··q⁺³ Fluorescence vs. Time

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TABLE III

Curve	Nd_2O_3 (wt.%)	τ_1 (long lifetime)	τ_2 (short lifetime)	τ_1/τ_2	I_{10}/I_{20}
A	1	1.37	.48	2.85	.293
B	2	1.09	.48	2.27	.325
C	4	.83	.43	1.93	.329
D	6	.57	.33	1.73	.43

If we assume that at low Nd_2O_3 concentrations there are more singly occupied (or uncoupled) sites than there are doubly occupied (or coupled) sites this leads to the following conclusions.

(1) Singly occupied sites have shorter lifetimes than doubly occupied sites since $I_{20}>I_{10}$ and $\tau_1>\tau_2$.

(2) As the Nd_2O_3 concentration increases I_{10}/I_{20} increase, i.e. there are proportionally more doubly occupied than singly occupied sites in the glass. This effect was not as large as one might expect intuitively, in fact the spread in values could possibly be explained away as the experimental error evolved in choosing the best straight line to fit the data points in the tail of the curve.

(3) Both τ_1 and τ_2 decrease as Nd_2O_3 concentration increases but the singly occupied sites appear to be much less effected initially. The accuracy of these values, which is less sensitive to curve fitting than the ratio I_{10}/I_{20}, is about ± 5%.

(4) As the Nd_2O_2 concentration increases and concentration quenching becomes more evident the ratio of τ_1/τ_2 approaches unity. This is as predicted since the individual neodymium sites are no longer completely independent and spatial transfer of excited electrons takes place between neighboring neodymium ions. Since both τ_1 and τ_2 decrease, an increase in the transition probability to non-radiative sites must be taking place which also contributes to the concentration quenching mechanisms.

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Some of the above conclusions should be considered tentative due
to the limited amounts of data involved. Further work would be
required to understand the situation more fully.

2.4   LASER THRESHOLD

        Evaluation has been completed on the new laser cavity
designed to produce reliable laser threshold data for small
experimental melts of glass containing varying degrees of stria.
The only change made in the system previously described[3] is that
the reflector on the transmitting end of the rod now consists of
a gold foil cap with an 0.011" diameter pinhole in it, as shown
in Fig. 9, rather than the Fresnel reflectance of the glass-to-air
interface.

        To check the effect of stria on this system a group of
1/2" diameter rods were cut from selected areas of a block of laser
glass so that they contained varying degrees of stria. Shadow-
graphs of these rods taken in both directions are shown in Fig. 10.
Threshold measurements made on 0.080" × 5-3/4" laser rods drawn
from these 1/2" rods are tabulated in Table IV.

TABLE IV

	Section A	Section B	Section C	Section D
	45 watt-sec	49 watt-sec	45 watt-sec	49 watt-sec
	45	45	42	45
	48	42	49	49
	45	42	45	49
	42	52	52	52
	42		45	52
Mean value	44.5	46	46.3	49.3
R.M.S. Deviation	2.10	3.96	3.24	2.35

The root-mean-square deviation from the mean value for each group
of laser rods is listed. The average value of the r.m.s. deviations
of the four groups is 2.9 watt-sec. This is a measure of the
reproducibility within a group of essentially identical laser rods.
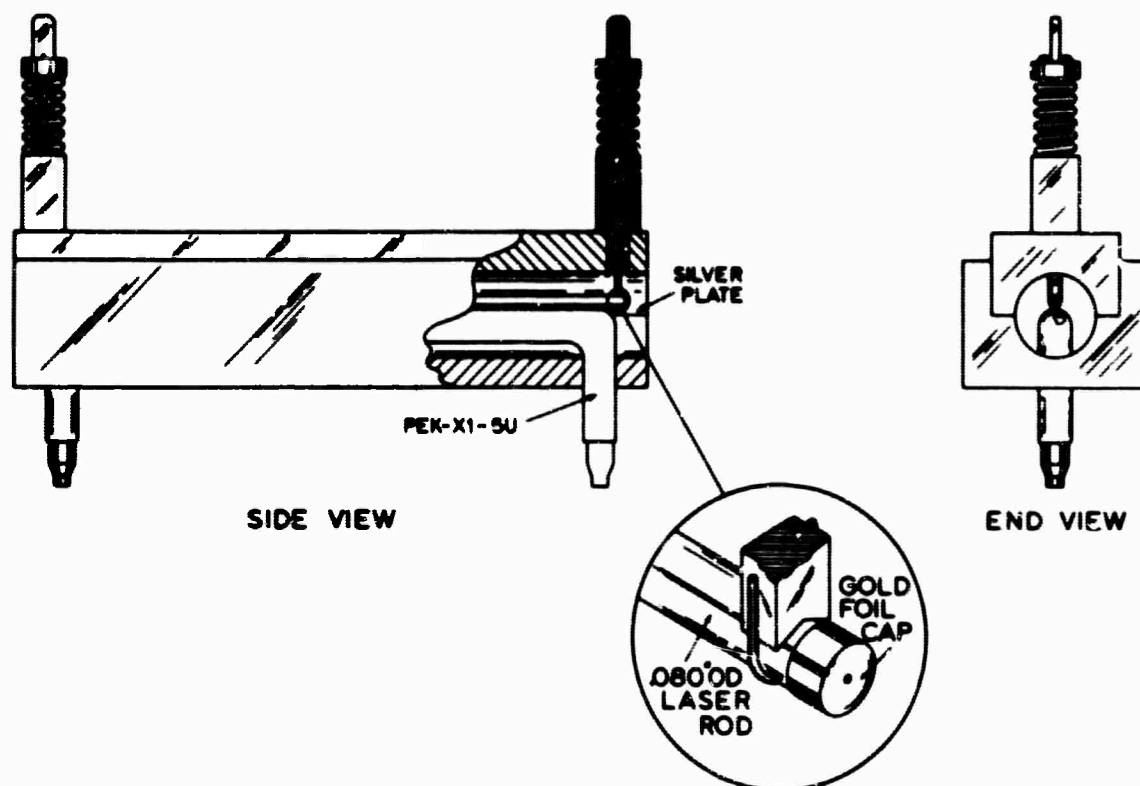
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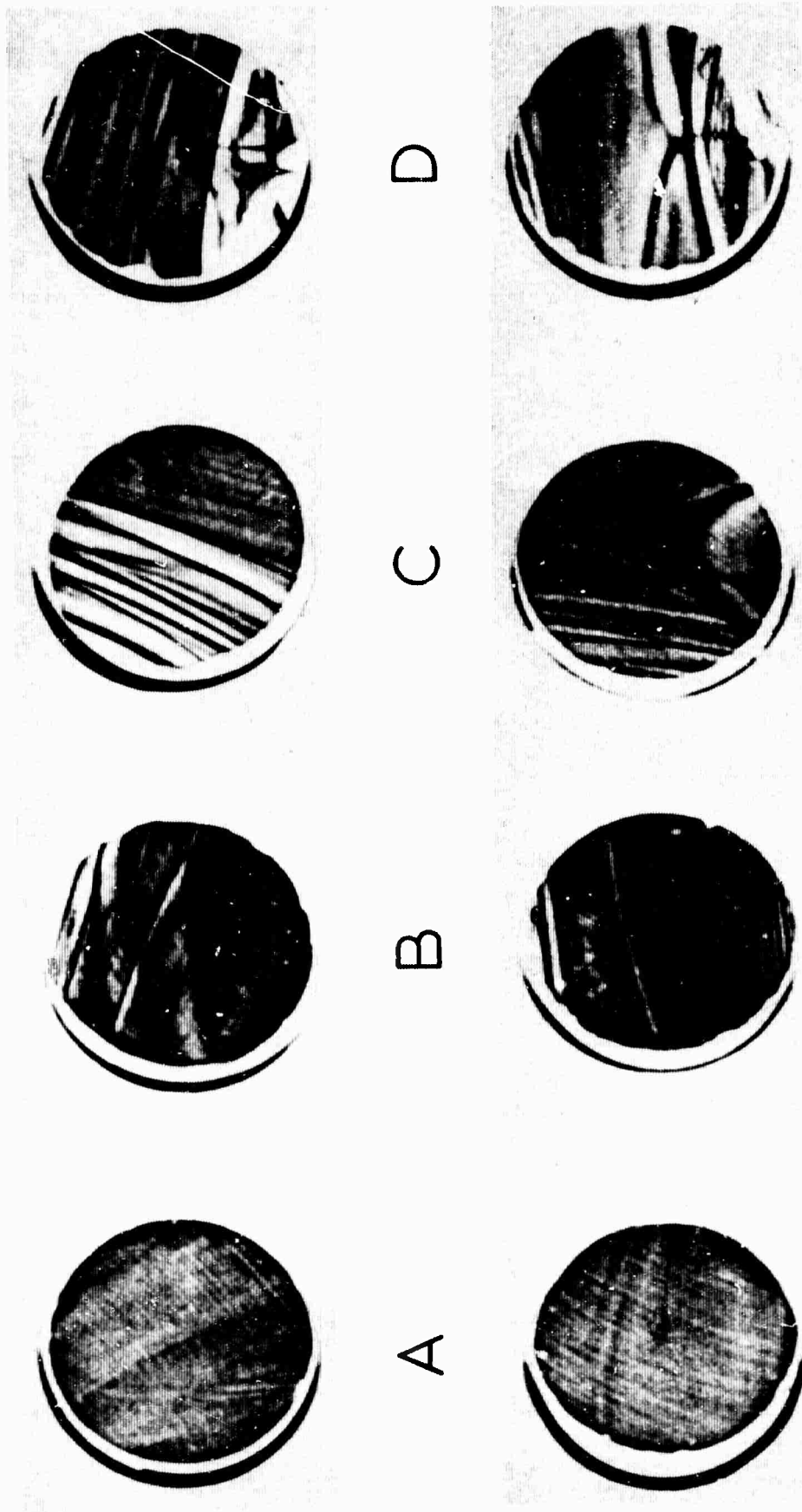Figure 9. Sketch of Laser Head for Threshold Determinations of Experimental Glasses.

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Figure 10. Shadowgraphs Showing the Varying Degrees of Stria in the Glass Samples Used for the Evaluation of the Laser Threshold Apparatus. Mag. 3×

Of primary interest is the r.m.s. deviation of all the threshold
values from the mean value of all 23 rods which is 3.4 watt-sec.
This value when compared with the above value of 2.9 watt-sec
indicates that the varying degrees of stria present in these
rods have very little effect on the threshold values measured
with this laser system.

A series of about fifty laser glasses selected to provide
varying compositions have had laser threshold measured with this
system. Preliminary examination of this data which was normalized
to take into account the effects of lifetime, neodymium concen-
tration and refraction index on population inversion, indicate
that there may also be a correlation between threshold and
composition. This data is now being analyzed more thoroughly.

No further contract effort will be spent in this area
after this analysis has been completed.

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1. Kreidl and Hensler, J. Am. Ceram. Soc. 38, No. 12, 423 (1955).

2. Ryosuki Yokota, Phys. Rev. 95, 1145-8 (1954).

3. Semi-Annual Report #3, ONR Contract No. Nonr-3835(00).